DRAFT

APPENDIX I. PYROLYSIS OF POLYURETHANE FOAM

This work was contracted with the US Army Aberdeen Test Center and coordinated by Dr. Steven H. Hoke of the Chromatography Analysis Division.

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APPLIED SCIENCES TEAM
CHEMISTRY UNIT

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Project Number: None

Report Number: 2004-CC-045
Title: Combustion of Foam Panels

Authorized for Release:

Signature Date: 13 November 2003

Judith D. Galloway
Chief, Chemistry Unit

CSTE-DTC-AT-WC-C (70-10r) 13 November 2003

MEMORANDUM FOR USACHPPM Chromatography Analysis Division,
ATTN: Steven H. Hoke, Ph.D

SUBJECT: Combustion of Foam Panels, Laboratory Report Number 2004-CC-045

1. References:

a. Chemistry Team Internal Operating Procedure No. 360, Operation of 760 Fourier Transform Infrared Spectrometer with MCT-A detector.

b. Chemistry Team Internal Operating Procedure No. 361, FTIR Analysis of Solids using the Brill Pyrolysis Cell.

2. Two samples from foam panels were received by the Chemistry Unit. The samples were assigned sample numbers 0310027-01 and 0310027-02. See Tables 1 and 2, Enclosure 2 below for sample descriptions. The combustion products given off when these foam panels burn has become a concern. Identification of combustion products in air (21% oxygen) was requested.

3. Initial work with these samples focused on identification of the foam and adhesive on the foam. Next the foam was pyrolized in nitrogen. The final analytical determination was combustion of the foam in air. Most of the identification analysis was performed with the Continuum microscope linked with a Thermo-Nicolet Magnum FTIR optical bench. Pyrolysis and combustion were performed with a CSD pyrolysis (Brill) cell fitted in the sample compartment of the FTIR bench.

4. The samples were received wet with water. They were air dried before analysis was begun. The identification analysis was performed using a FTIR spectrometer and an Attenuated Total Reflectance accessory (ATR) and the infrared microscope accessory (Thermo Continuum). The photographs and infrared spectra are in Figures 1 to 10, Enclosure 3.

5. Identification of the foam type was performed by running the infrared spectrum of the unburned foam sample 0310027-01 (Figures 1 and 2). The spectrum produced (Figure 3.) closely matched polyester urethane foam (Figure 4.). Since foam is a polymer product made with various monomers in various ratios an exact match is not possible. This match shows the basic components that make up the bulk of the material. This foam is therefore a polyester urethane co-polymer product.

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6. The picture of a foam cell in Figure 2 shows that each cell is covered with a thick oily liquid. This liquid is not visible to the naked eye as shown in the picture in Figure 1. Identification of this liquid is essential as it is a significant component of the foam. The spectrum produced by the liquid (Figure 5.) closely matched polypropylene glycol (Figure 6.).

7. Figure 7 is a picture of the burned foam sample 0310027-02 with adhesive on the outer surface. The adhesive side of the foam was positioned against the ATR accessory and the infrared spectrum acquired (Figure 8). The library search produced the match seen in Figure 9. The best match is a latex rubber based mineral filled adhesive. A second library search was performed against a library of minerals and the library match shown in figure 10 was produced. The mineral filling in the adhesive is a silicate class compound similar to the natural mineral Kaolinite (see information with Figure 10).

8. The identification of the combustion products produced by the foam sample 0310027-01 was determined using Pyrolysis/Fourier Transform Infrared (FTIR) spectroscopy (reference 1a and 1b). See Enclosure 1 for an explanation of this technique. This type of analysis involves rapidly heating a small amount of the sample and monitoring the gas phase above the heated sample with FTIR spectroscopy. Gas products were identified using a Nicolet 760 FTIR spectrometer with an MCT-A detector. The sample was pyrolyzed (reference 1b) in a CDS Brill Cell, which fits into the sample compartment of the FTIR spectrometer so the gas products from heating could be identified in near real-time. The Brill Cell was connected to a CDS 2000 Pyrolyzer equipped with a CDS FTIR probe rod. The probe rod contains a small electrically heated ribbon upon which the samples were placed. (The ribbon can be heated up to 1350^{o}C at a variety of heating rates from 1 ^{o}C/min to 1,000,000 ^{o}C/sec. The samples (~2 mg each) were heated at 20 ^{o}C for 2 seconds then heated at a rate of 300 ^{o}C/second up to 1000 ^{o}C and held at 1000 ^{o}C for 30 seconds for this combustion study. Pyrolysis was also performed on these samples. Plots of the evolved gas phase spectra were then made. The gas spectra were searched against a database and identified.

9. Infrared spectra of pyrolysis and combustion of the samples are in Figures 11 through 19, Enclosure 3. Descriptive data on the samples is in Tables 1 and 2, Enclosure 2. Identification of the pyrolysis and combustion products is in Table 3. Since the two foam samples were identical only samples 0310027-01 was pyrolized and combusted.

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10. Pyrolysis occurs when the sample is heated in a 100% nitrogen atmosphere. Initial pyrolysis products are produced about 8 seconds into the 30 second heating time. Initial products frequently contain vaporized parent molecules (the starting compound). Final pyrolysis products are what are present at the end of the run (29 to 31 seconds). The parent molecule is often converted completely into lighter weight molecules by this time.

11. The pyrolysis of foam is shown in Figures 11 to 14. The fully pyrolized foam is displayed in figure 11. A large absorption at ~2270 cm^{-1} is produced in this spectrum. The best library match; methyl isocyanate, is shown in figure 12. Figure 13 is the infrared spectrum of the pyrolized foam with all of the major absorption peaks labeled. Note that due to a lack of oxygen the amounts of carbon dioxide and carbon monoxide are low.

12. Figure 14 shows the foam pyrolysis progression. Initially the isocyanate compound (which is thought to be a mixture of C1 to C4 isocyanates) and foam vapor is detected, next carbon monoxide and carbon dioxide are formed from the foam vapor. The final pyrolysis products are an Isocyanate Compound (H_yC_xNCO), and much lesser quantities of Carbon Dioxide (CO_2), Carbon Monoxide (CO), Ethylene (C_2H_4), Acetylene (C_2H_2), Hydrogen Cyanide (HCN) and Vaporized Foam. The more oxygen starved the combustion of foam the more the gases produced will favor the final pyrolysis products. Not all of the foam is consumed in this pyrolysis. See Enclosure 4 for more information on the reaction mechanism and isocyanate compounds.

13. Combustion occurs when the sample is heated in an oxygen atmosphere. Initial combustion products are produced about 8 seconds into the 30 second heating time. Initial products frequently contain vaporized parent molecules (the starting compound). Final combustion products are what are present at the end of the run (29 to 31 seconds). The parent molecule is often converted completely into carbon dioxide and water vapor by this time.

14. The combustion of the foam is shown in Figures 15 through 18. The fully combusted foam is displayed in figure 15. A large absorption at ~2270 cm^{-1} is produced in this spectrum. The best library match; an isocyanate compound, is shown in figure 16 along with the major gases that are produced in this combustion. Figure 17 is the infrared spectrum of the pyrolized foam with all of the major absorption peaks labeled.

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15. Figure 18 shows the foam combustion progression. The initial combustion products are the isocyanate compound (which is thought to be a mixture of C1 to C4 isocyanates) and foam vapor. At this point (about 6 seconds into the combustion) the products are the same as pyrolysis. As the combustion progresses (see middle and lower spectra on Figure 18.) large quantities of carbon dioxide and carbon monaoxide are produced. The final products are the Isocyanate Compound (H_yC_xNCO), Carbon Dioxide (CO_2), Carbon Monoxide (CO), Methane (CH_4), Ethylene (C_2H_4), Acetylene (C_2H_2), Hydrogen Cyanide (HCN), and Vaporized Foam. Combustion is incomplete as evidenced by the presents of carbon monoxide and foam vapor. See Enclosure 4 for more information on the reaction mechanism and isocyanate compounds.

16. Figure 19 is included to show some of the major functional chemical groups in the original foam. The aliphatic hydrocarbons produce Methane (CH_4), Ethylene (C_2H_4), Acetylene (C_2H_2), as they break down into smaller molecules during combustion. As these smaller molecules are oxidized (combusted) they form Carbon Dioxide (CO_2) and Carbon Monoxide (CO). The isocyanate compound is released from the polymer backbone by the heat of combustion and forms the mixture of C1 to C4 isocyanates. The nitrile compound is the most likely source of the hydrogen cyanide. The ester and urethane (not labeled) parts of the foam also form isocyanates (see enclosure 4 explanation of thermal degradation mechanisms). All other parts on the foam contribute to the Carbon Dioxide (CO_2) and Carbon Monoxide (CO) seen in the combustion sepctra.

17. The POC for this report is Paul Marsh, (410) 278-3024.

Enclosure 1.

Analytical Method: Fourier Transform Infrared Spectroscopy With Brill Pyrolysis Cell

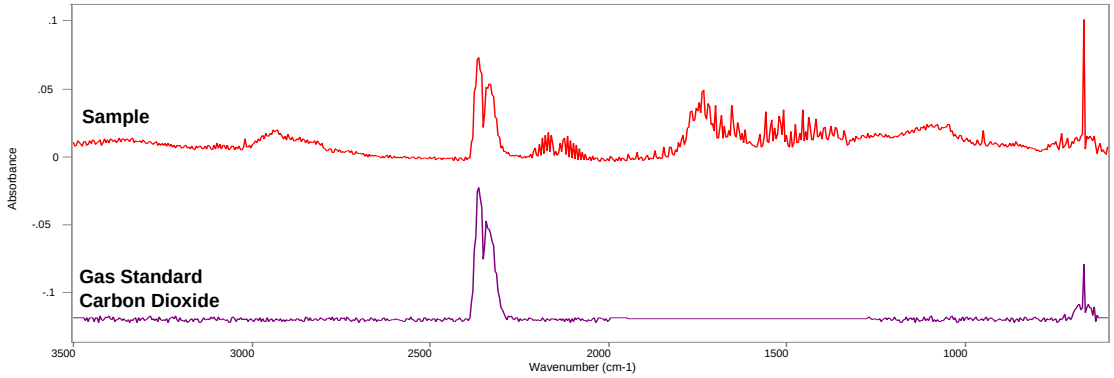
Fourier transform infrared spectroscopy (FTIR) is an analytical technique that exploits the infrared light absorbing characteristics of chemical compounds. Most major chemical functional groups i.e., alcohols, hydrocarbons, ethers etc., have specific absorption bands in the infrared region of the light spectrum. From noting which infrared frequencies a sample absorbs, the chemical structure of a sample can be determined. Quantitative information can be determined from the intensity of the absorption bands.

An FTIR spectrophotometer is the instrument used to scan the infrared light region. The instrument produces a plot of absorption vs. infrared frequency. The major parts of an FTIR spectrophotometer with Brill Pyrolysis Cell are as follows:

1. Source of infrared light (glowbar)
2. Interferometer (frequency modulator)
3. Brill pyrolysis Gas Cell (sample is held in the cell) with heated probe
4. Detector of infrared light (MCT semiconductor)
5. Computer controller with Data Base of infrared spectra

The Brill Pyrolysis Cell is an accessory that fits into the sample compartment of the FTIR spectrometer. The accessory has two parts the gas cell and pyrolysis probe. The pyrolysis probe has a filament (ribbon) that can be rapidly heated to greater than 1000 degrees Celsius. The sample is placed on this ribbon and the probe is placed in the gas cell. The gas cell is a fixed volume container that holds all the gases produced by the pyrolysis of the sample. The atmosphere in the cell can be selected to match the experiment i.e. nitrogen for pyrolysis or nitrogen oxygen mixture for combustion. The cell can be set for static or dynamic flow. The infrared beam passes through the cell and the gases are detected by the FTIR.

To determine the chemical makeup of samples, they must be compared to reference standards. Libraries of gas samples are available to identify the gases detected.



Enclosure 2.

Table 1. Foam Sample Identification

Sample Number	**Common Name**	**Description**
0310027-01	Gray polyester urethane foam	New Unburned foam
0310027-02	Gray polyester urethane foam	Piece 1 Foam with adhesive Piece 2 Burned Foam

Table 2. Foam Sample Descriptions

Sample Number	**Description**
0310027-01	RI1 Northwall Unburned 9/5/03
0310027-02	RI1Drummer's Box Burnt Foam 9/5/03

Table 3. Foam Pyrolysis and Combustion Products

Sample Number	**Test**	**Expected Combustion Products**
0310027-01	**Pyrolysis**	Isocyanate Compound (H_xC_xNCO), Carbon Dioxide (CO_2), Carbon Monoxide (CO), Ethylene (C_2H_4), Acetylene (C_2H_2), Hydrogen Cyanide (HCN), Vaporized Foam
0310027-01	**Combustion**	Isocyanate Compound (H_xC_xNCO), Carbon Dioxide (CO_2), Carbon Monoxide (CO), Methane (CH_4), Ethylene (C_2H_4), Acetylene (C_2H_2), Hydrogen Cyanide (HCN), Vaporized Foam

Enclosure 3.

Identification

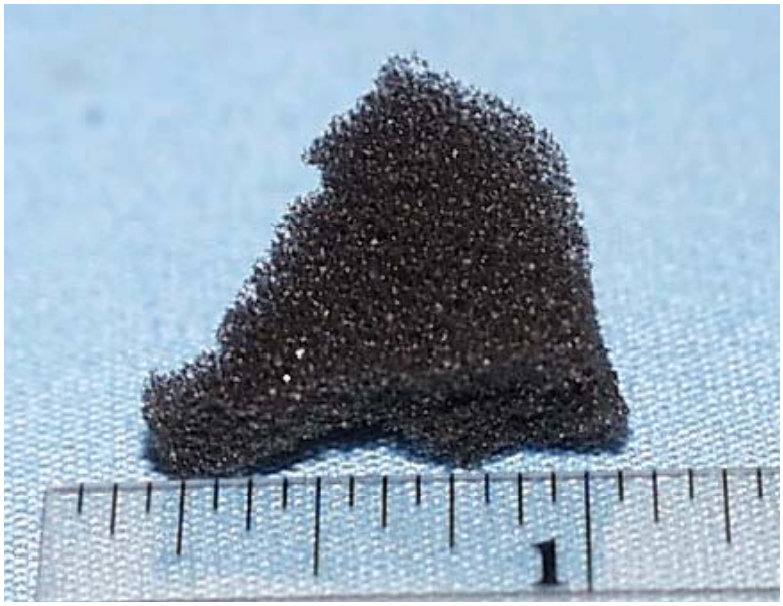


Figure 1. Sample 0310027-01 unburned foam.

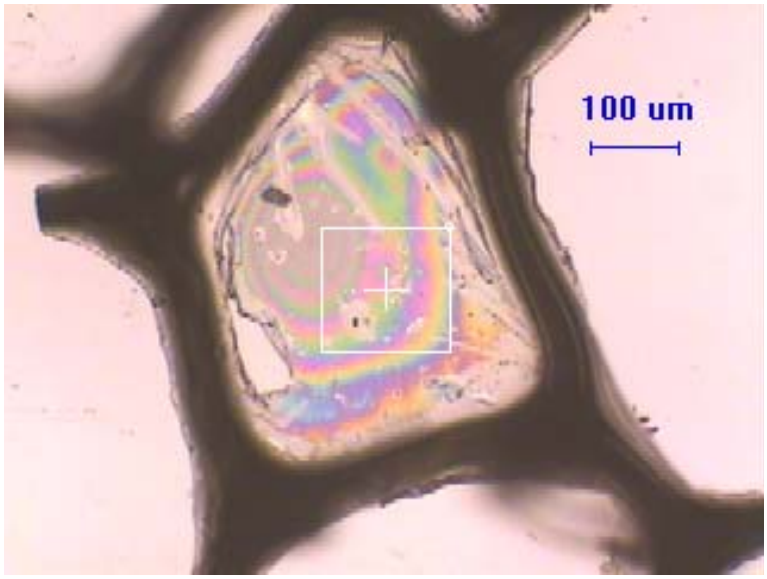


Figure 2. Microscope picture of sample 0310027-01 unburned foam at 100X magnification. This is a picture of one foam cell. All of the foam cells outer edges are covered in a thick clear liquid. This cell has the liquid actually spanning the open area of the cell.

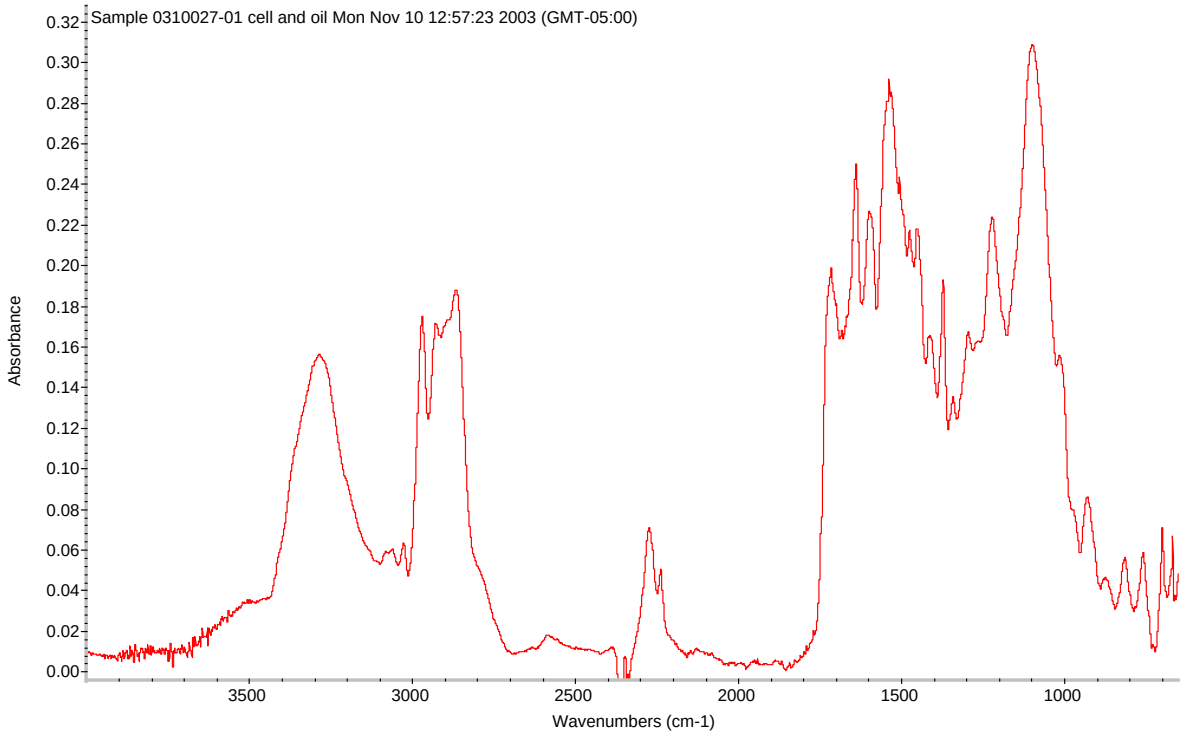


Figure 3. Infrared spectrum of sample unburned gray foam.

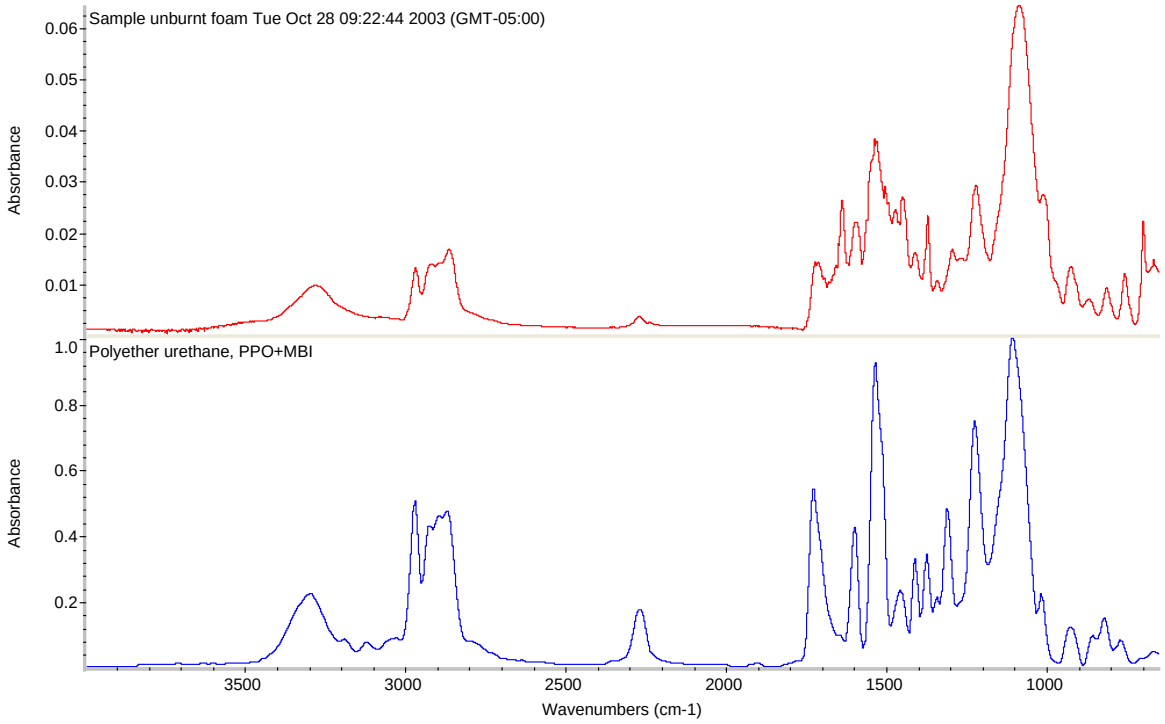


Figure 4. Infrared spectrum of sample unburned gray foam (top), best library match polyester urethane foam (bottom).

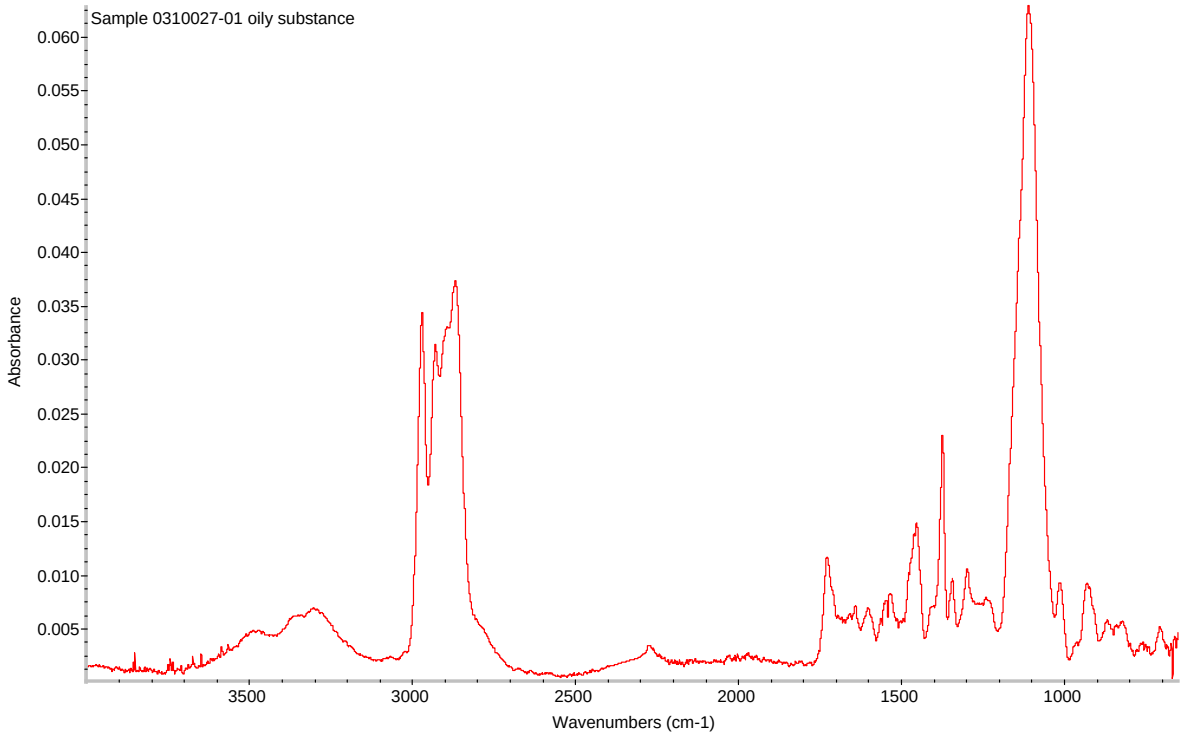


Figure 5. Infrared spectrum of sample oil on unburned gray foam.

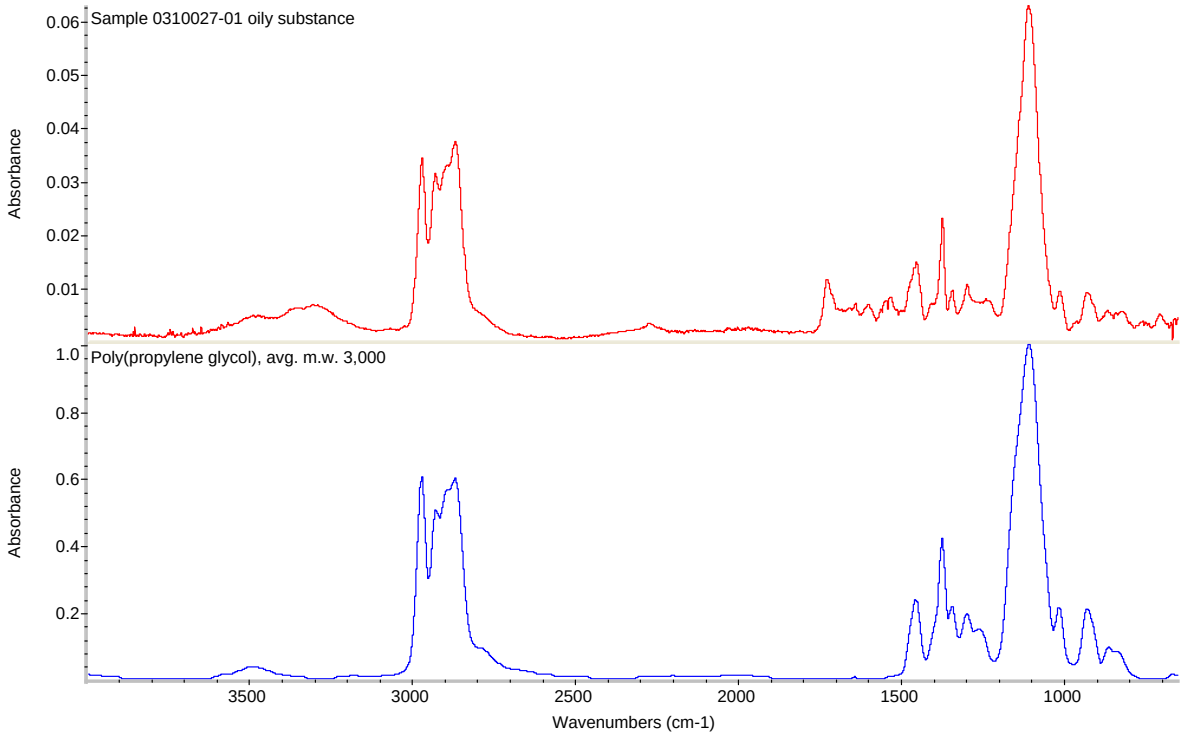


Figure 6. Infrared spectrum of sample oil on unburned gray foam (top), best library match polypropylene glycol (bottom).

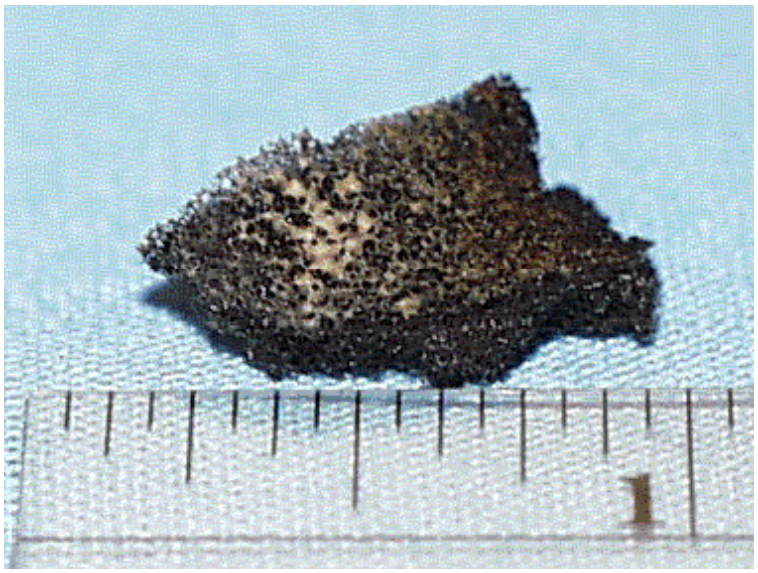


Figure 7. Sample 0310027-02 piece1 foam with adhesive.

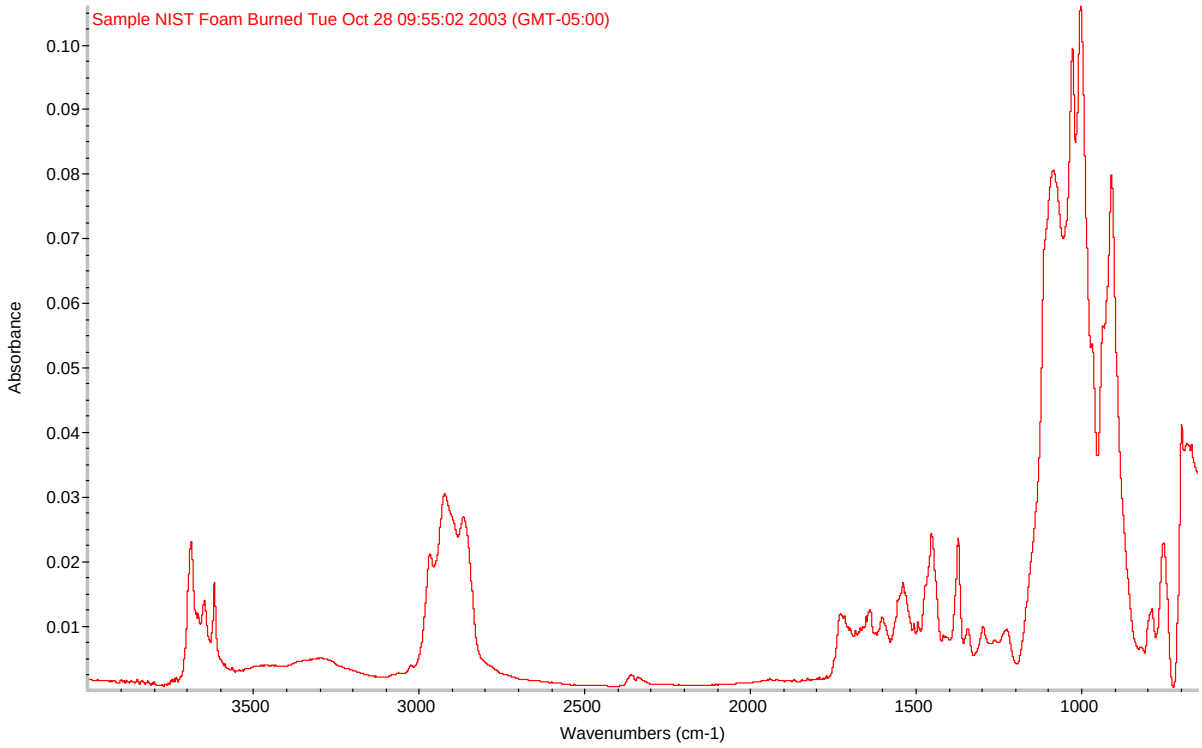


Figure 8. Infrared spectrum of sample foam adhesive.

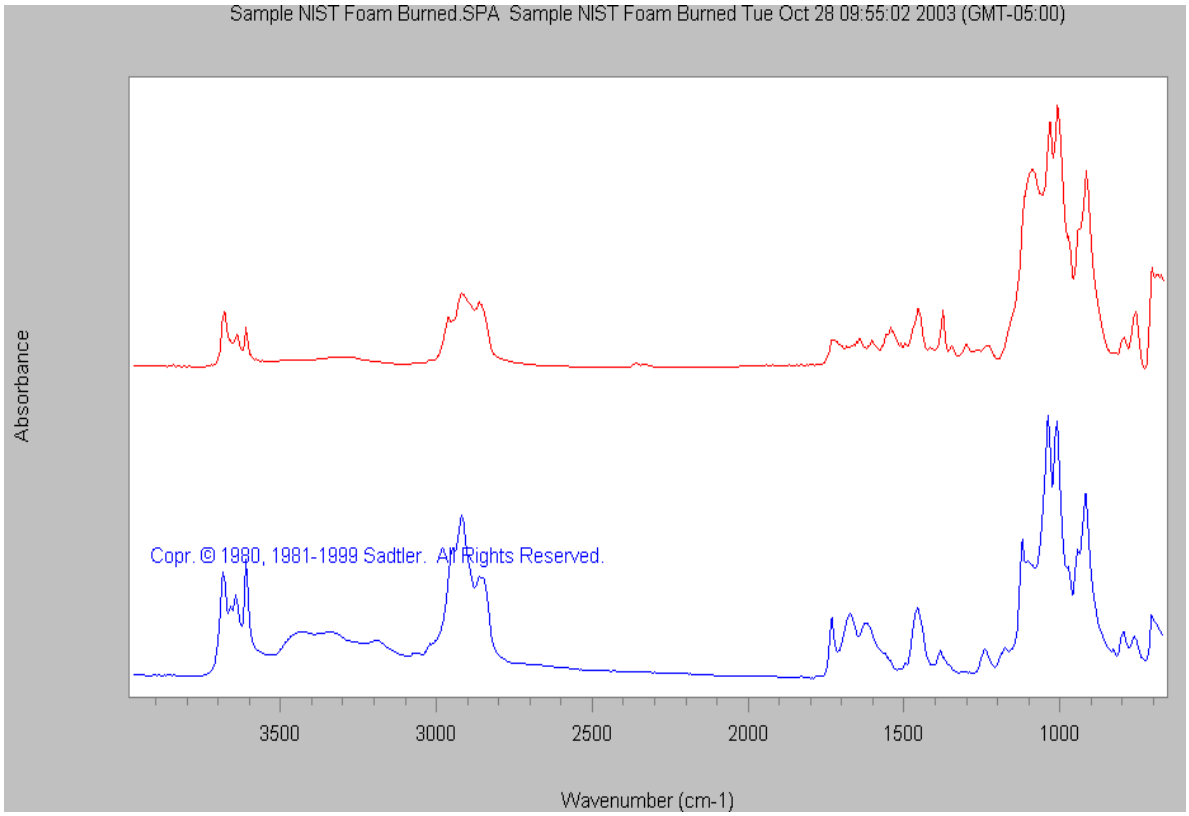


Figure 9. Infrared spectrum of foam adhesive (top), best library match a mineral filled latex based adhesive (bottom).

Database Information:
WELDWOOD MULTI-PURPOSE FLOOR ADHESIVE

Chemical Description= LATEX-BASED ADHESIVE
Content= Solids Content= 55%
Density= (Specific Gravity)= 1.17 g/ml
FlashPt= (PMCC) 100 ^{o}C Flash and Fire
Weight= 9.5 LBS/GAL

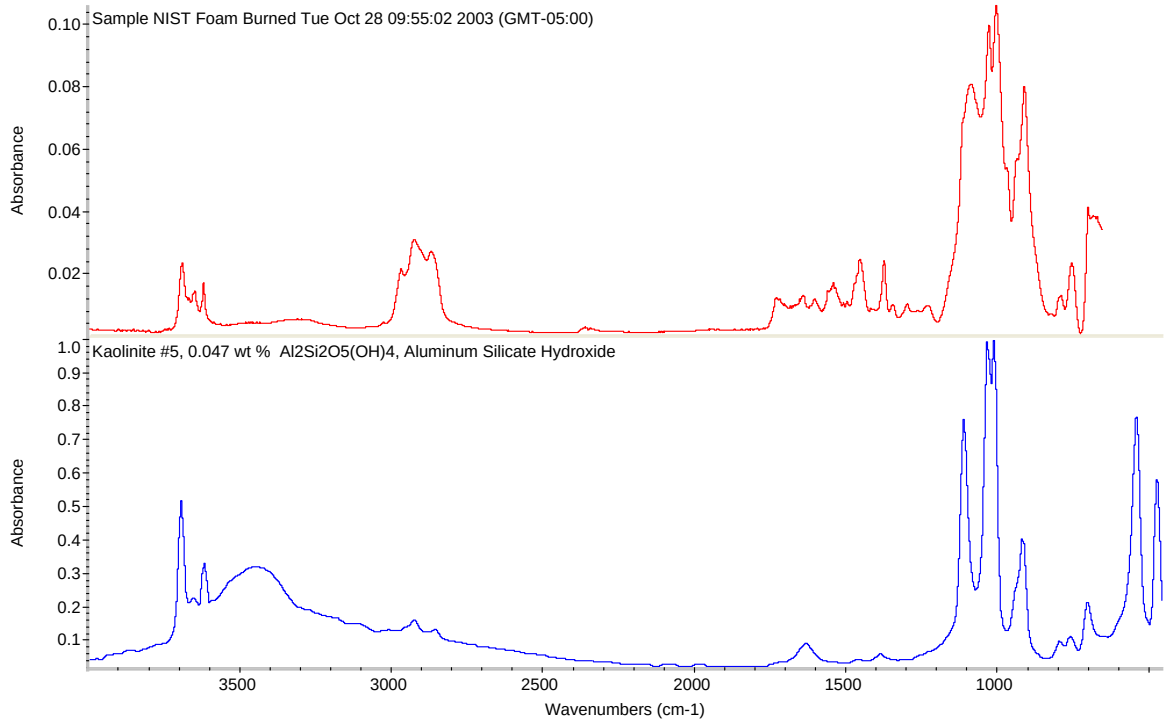


Figure 10. Infrared spectrum of sample foam adhesive (top), best library match of the mineral filler kaolinite $Al_2Si_2O_5(OH)_4$, (bottom).

Database Information on KAOLINITE

:

- **<u>Chemistry:</u> $Al_2Si_2O_5(OH)_4$, Aluminum Silicate Hydroxide**
- **<u>Uses:</u> In the production of ceramics, as a filler for paint, rubber and plastics and the largest use is in the paper industry to produce a glossy paper such as is used in most magazines.**

Pyrolysis

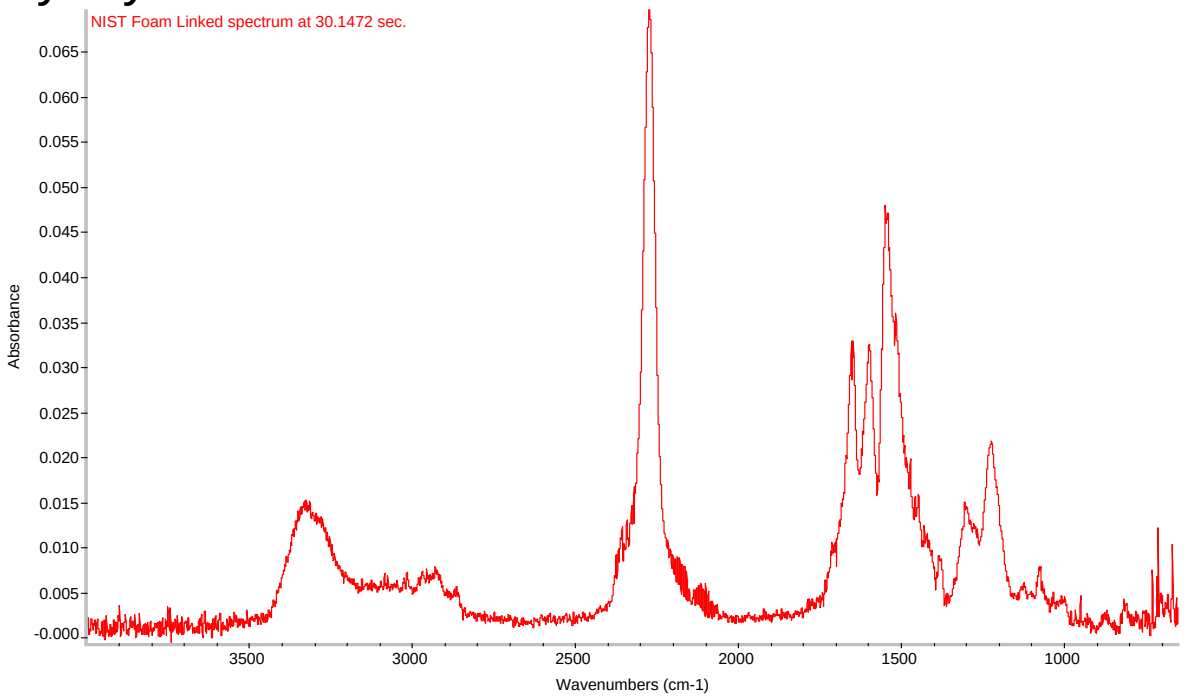


Figure 11. Infrared spectrum of Foam Pyrolysis. The isocyanate peak 2270 cm^{-1} is from a class of compounds with the general formula H_xC_xHNO. These compounds are very toxic.

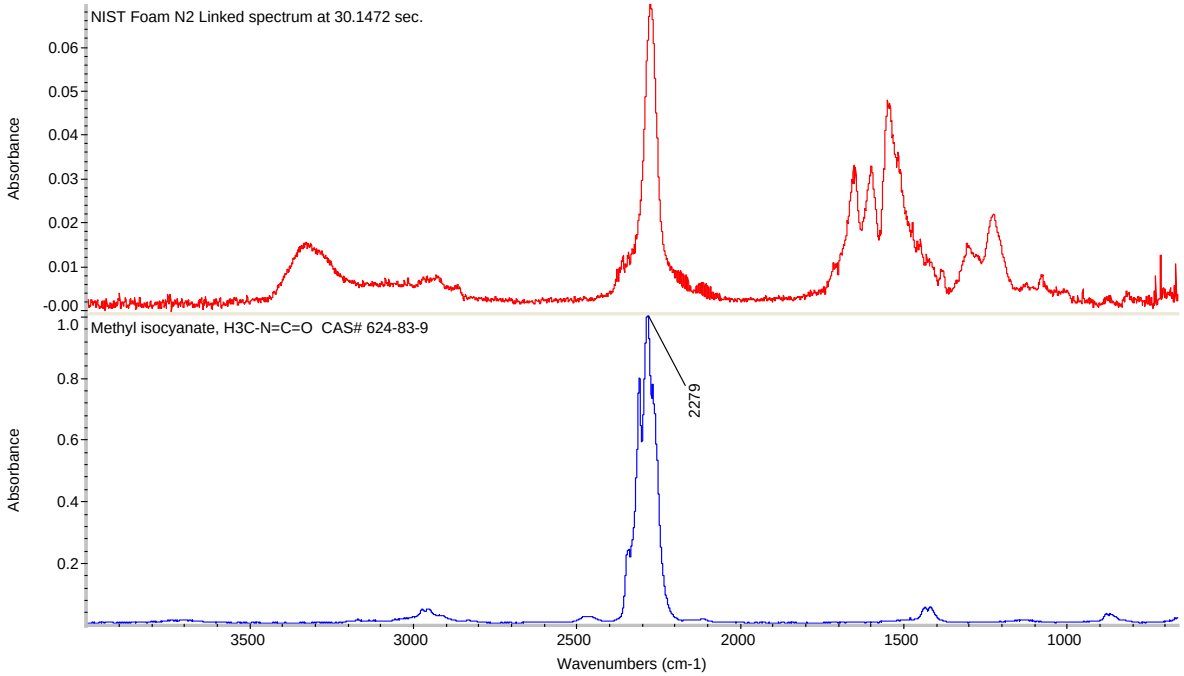


Figure 12. Infrared spectrum of sample pyrolized foam (top). Best library match is methyl isocyanate (peak ~2270 cm^{-1}). This is a match to a class of isocyanate compounds. Methyl, Propyl, and even Butyl isocyanate have spectra that cannot be distinguished at this resolution.

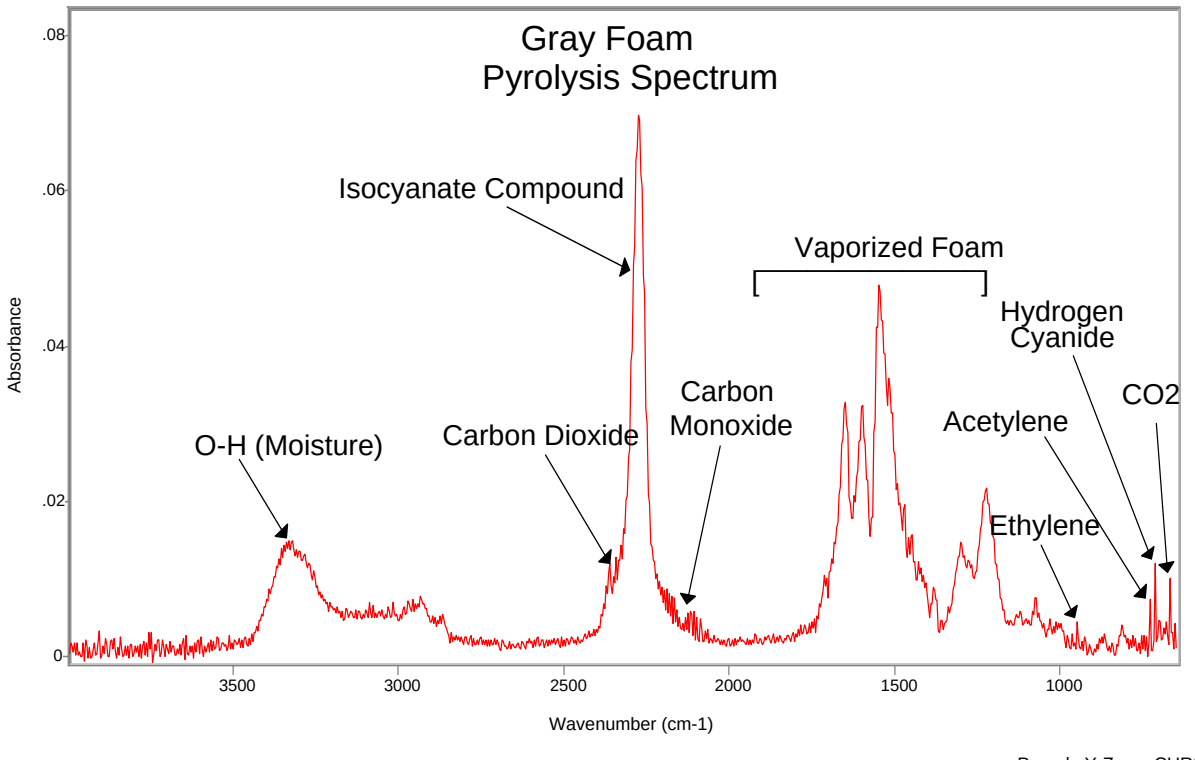


Figure 13. Infrared spectrum of gray foam pyrolysis with gases labeled. The more oxygen starved the combustion the more the final products will be similar to the pyrolysis products.

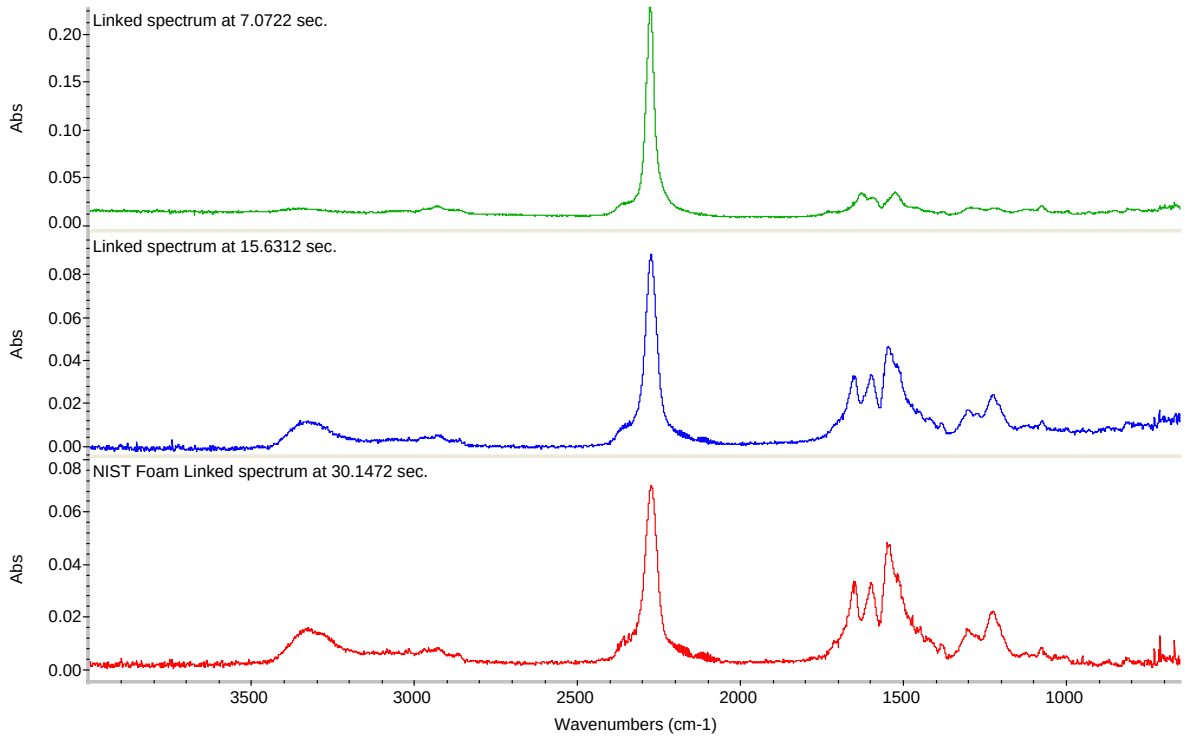


Figure 14. Infrared spectrum of Foam pyrolysis progression.

Combustion

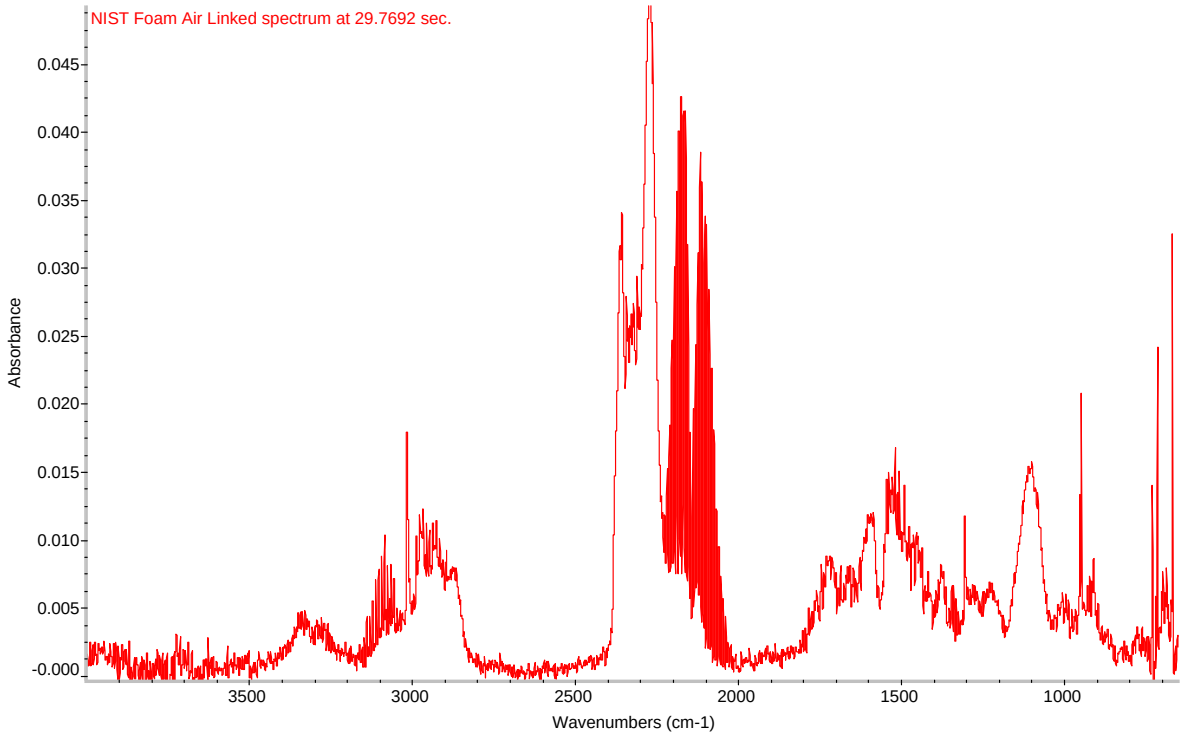


Figure 15. Infrared spectrum of Foam Combustion in air.

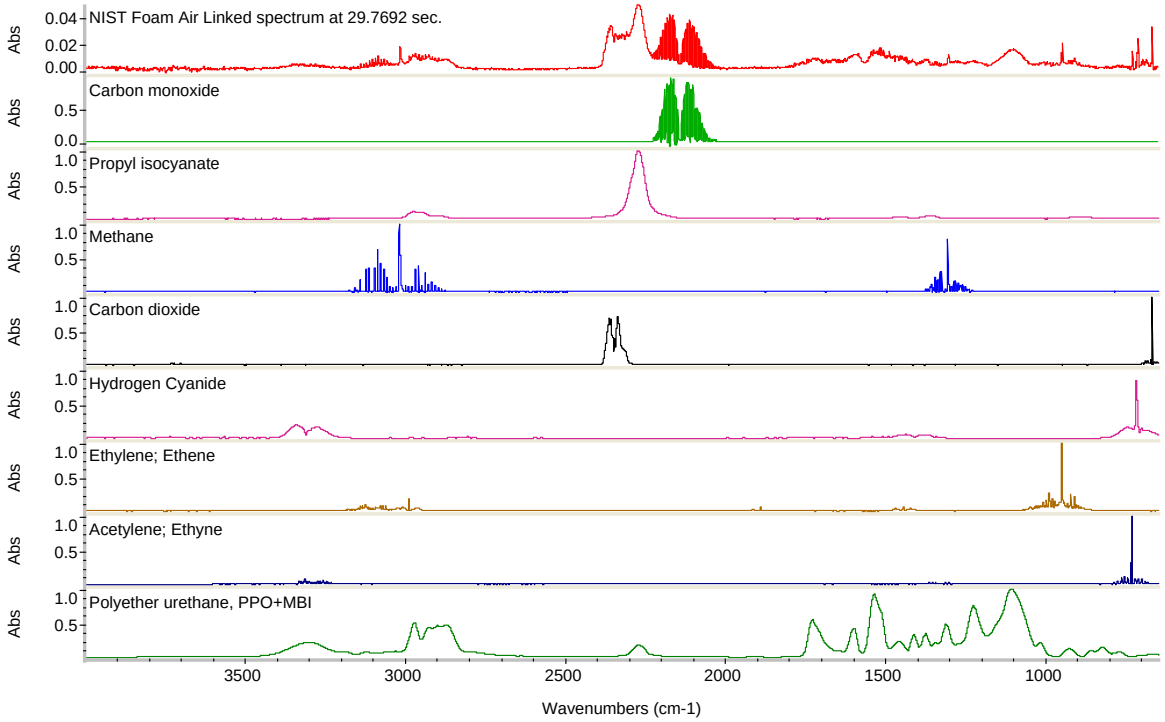


Figure 16. Infrared spectrum of Foam Combustion (top) and identified gases below.

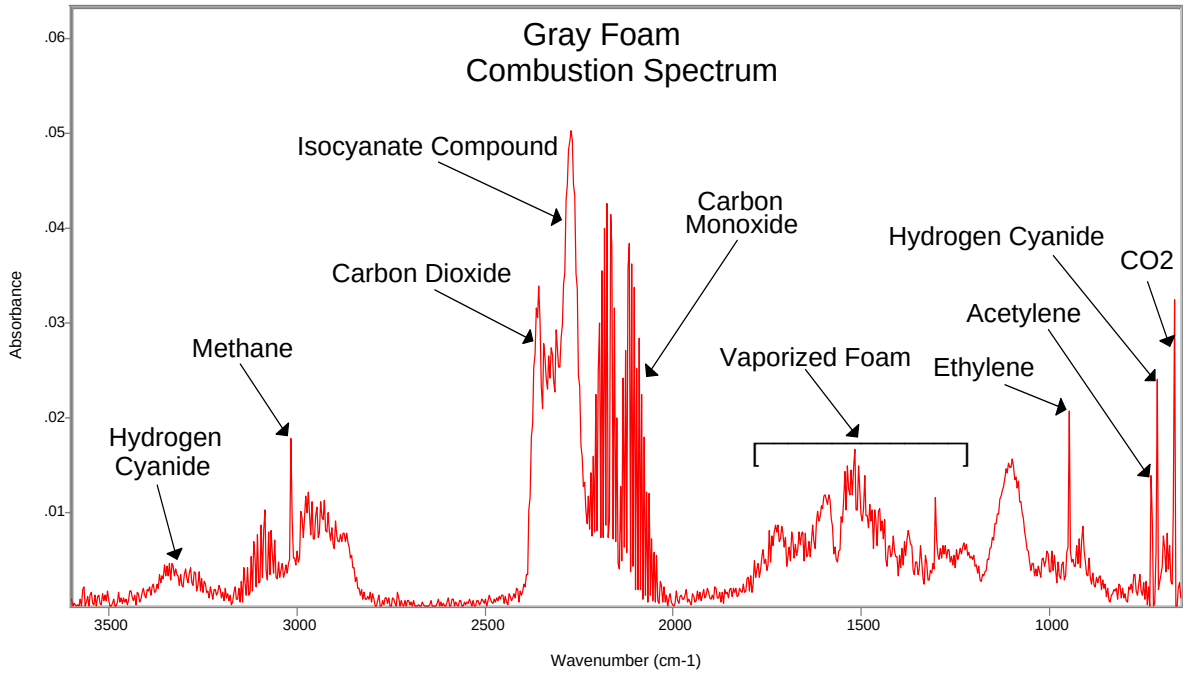


Figure 17. Infrared spectrum of Gray foam combustion with combustion gases labeled

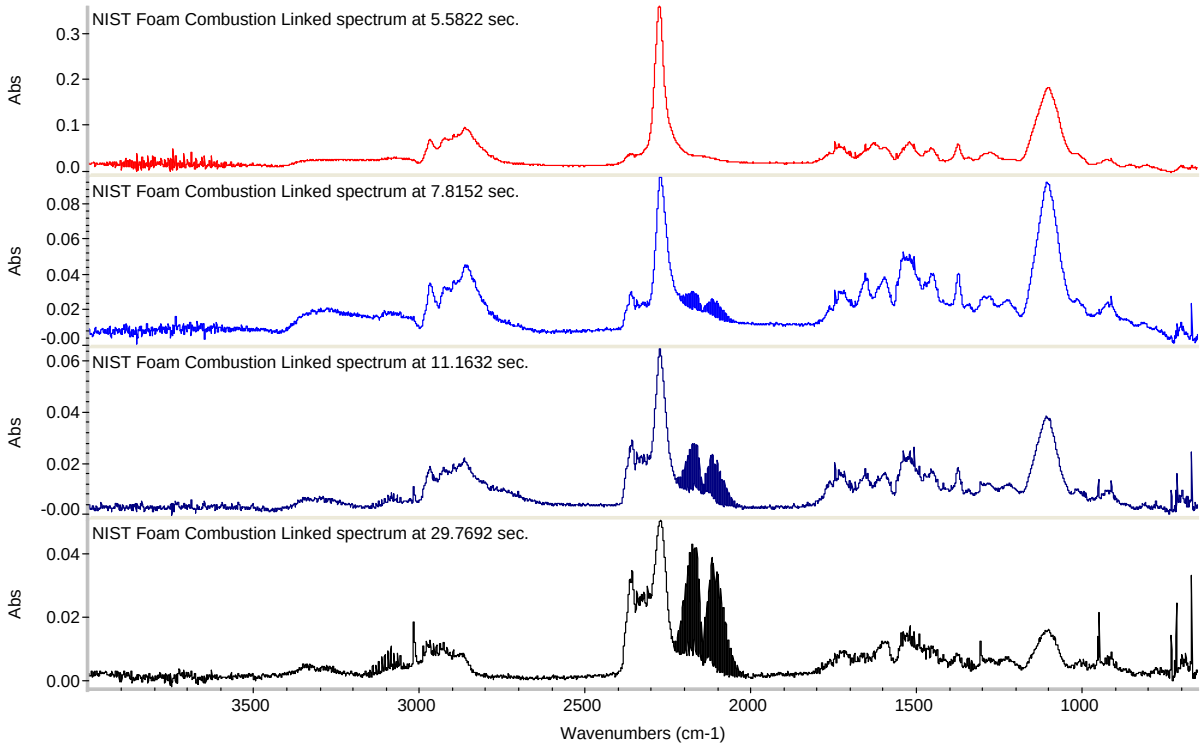


Figure 18. Infrared spectrum of Foam Combustion progression. Note the growth of the carbon monoxide peak (centered at 2150 cm^{-1}) as the combustion progresses from 5 to 30 seconds. The isocyantate compound peak (~2270 cm^{-1}) dominates each spectrum. The polypropylene peak (~1100 cm^{-1}) is decreasing showing that the oily polypropylene (glycol?) compound is being consumed as the combustion progresses.

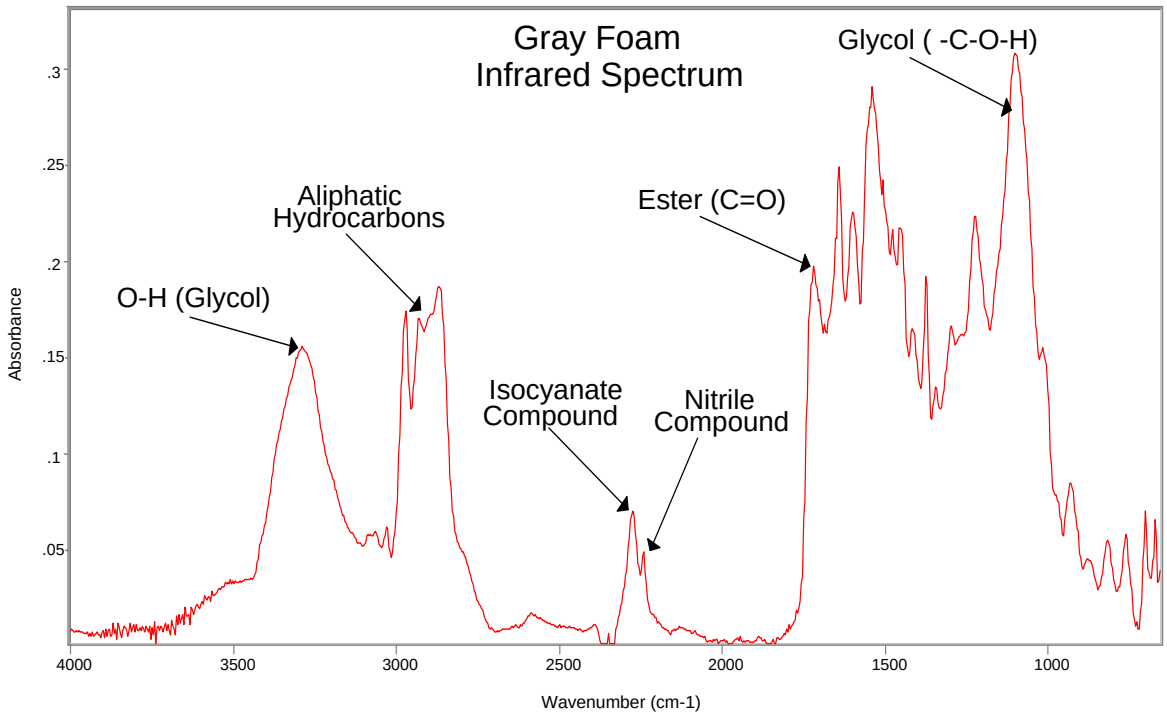
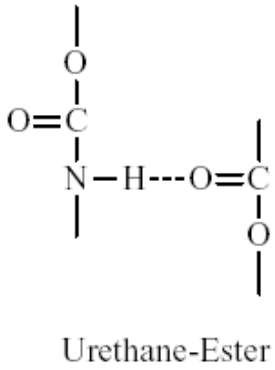


Figure 19. Infrared spectrum of gray polyether urethane foam with major structures labeled.

Enclosure 4.

Background Information:

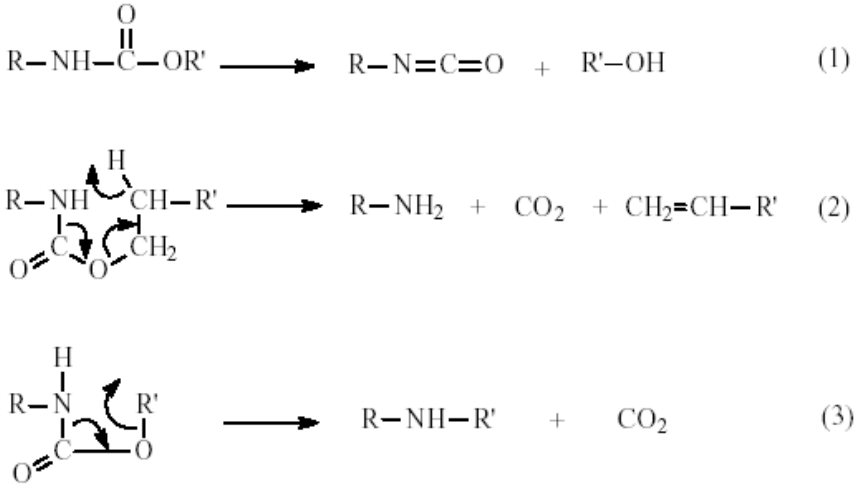


Urethane-Ester

Figure 1. Basic chemical structure of polyester urethane foam.

The chemical structure of the foam as shown in Figure 1 consists of two parts. The left side of the figure shows the urethane (OC=ONH) structure, the right side shows the ester (OC=O) structure.

The thermal degradation mechanism of polyurethane is very complicated. It has been suggested that polyurethanes break down by a combination of three independent pathways: (1) dissociation to the original polyol and isocyanate; (2) formation of a primary amine, an alkene, and a carbon dioxide in a concerted reaction involving a six-membered cyclic transition state; (3) formation of a secondary amine and carbon dioxide through a four-membered ring transition state, as shown in Scheme 2.2.[143-147]



Reference: pg. 50 of http://scholar.lib.vt.edu/theses/available/etd-72698-13572/unrestricted/Disswhl2.pdf

From the referenced combustion mechanism above pathway 1 which produces isocyanates must be the dominant combustion pathway. The large isocyanate peak in both the pyrolysis and combustion spectra of Figure 2 support this.

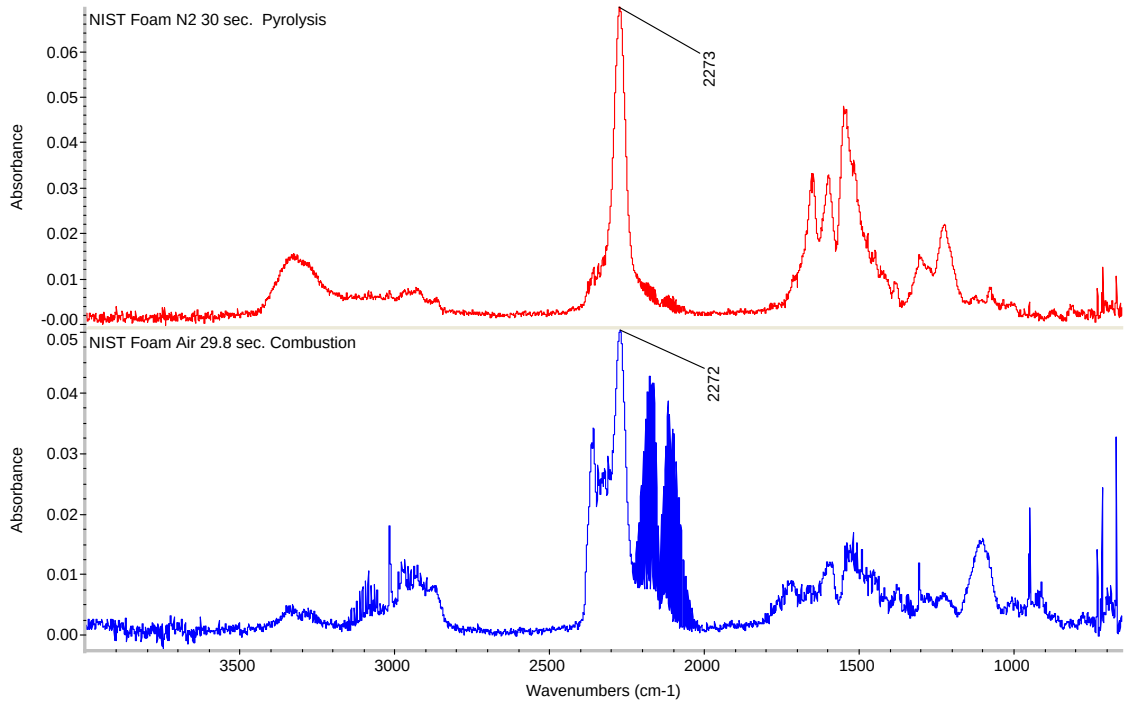


Figure 2. Infrared spectrum of foam pyrolysis gases (top) and combustion gases (bottom). The dominate peak in each spectrum is the peak at ~2270 cm^{-1}). This peak most closely matches isocyanate compounds (see figure 3). The related isocyanide compounds are not a good match (see figure 4) because their absorbance is too far from 2270 cm^{-1}.

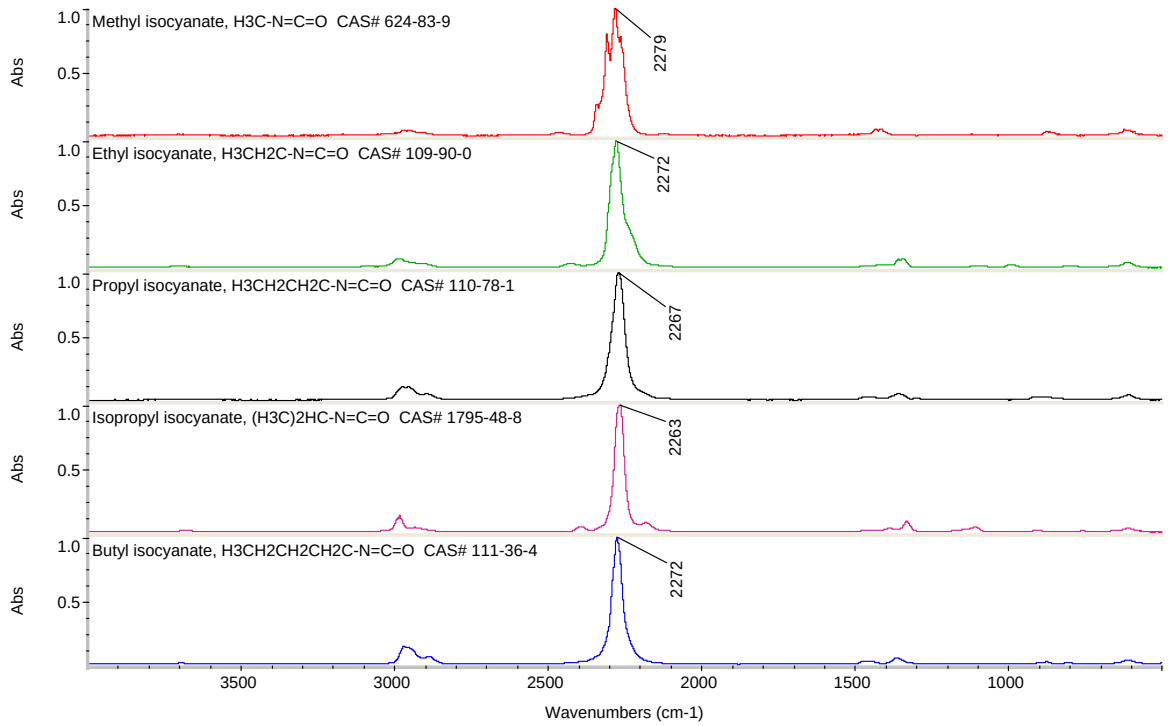


Figure 3. Infrared spectra of selected isocyanate compounds all with absorbance's in the 2270 +/- 9 cm^{-1} range. These are some of the most likely compounds to match the 2270 cm^{-1} peak in the pyrolysis and combustion spectra (Figure 2.).

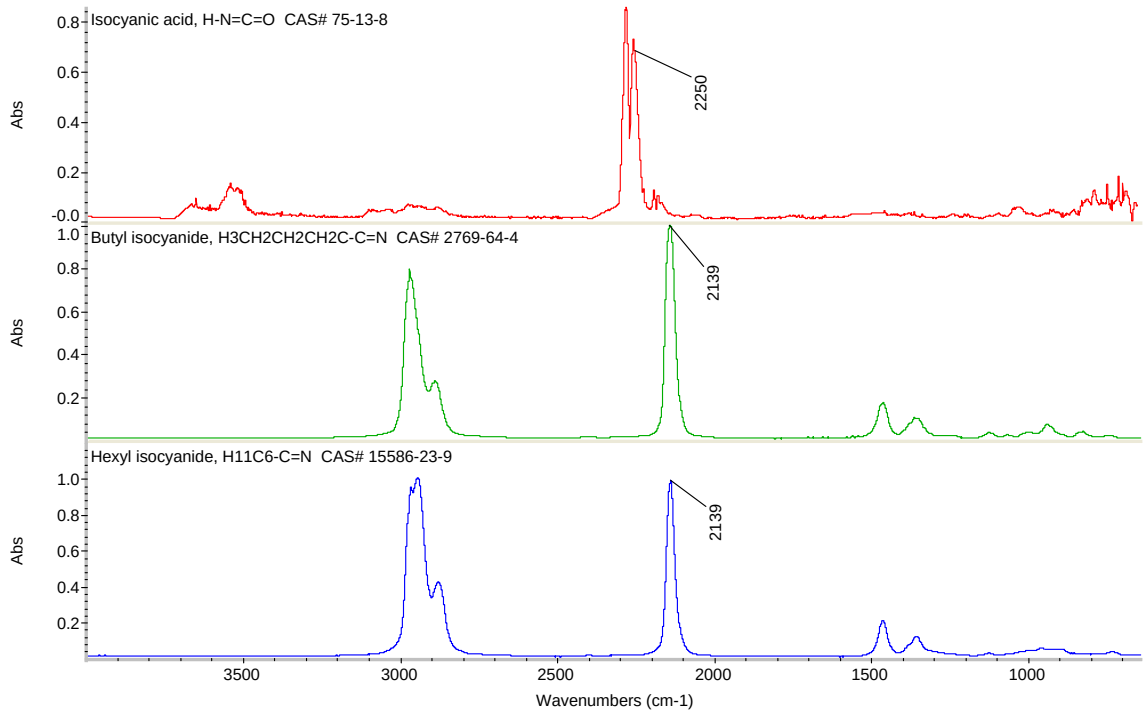


Figure 4. Infrared spectra of selected isocyanide compounds. These have a slightly different structure than the isocyanate compounds in Figure 3. These do not match the 2270 cm^{-1} peak in the pyrolysis and combustion spectra (Figure 2.).